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The determination of hafnium and zirconium in meteorites by neutron activation analysis

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THERE have hitherto been very few analyses upon which to base estimates of the abundances of hafnium and zirconium in iron and stone meteorites, (PINSON *et al.*, 1953), HEVESY and WÜRSTLIN, 1934, NODDACK, 1930). In our search for so-called extinct natural radioactivity our interests are now concentrated on the recently discovered long-lived Hf^{182} (MERZ, 1960; HUTCHIN and LINDNER, 1961) which decays through Ta^{182} to the stable isotope W^{182}. Since hafnium is lithophile and tungsten is siderophile, the concentration of W^{182} might be enhanced in stone meteorites.

In nature, hafnium is always accompanied by a large excess of zirconium. The great chemical similarity of hafnium and zirconium makes the chemical separation and accurate determination of both elements, when present in small amounts, extremely difficult. We have developed a procedure for determining these two elements together, without chemical separation, by means of neutron activation, measuring the induced activities of the nuclides Hf^{181} and Zr^{95} by pulse height analysis.

Samples weighing about 1 gram for each determination were sealed in silica ampoules and irradiated for 10 days in the BEPO reactor of the Atomic Energy Research Establishment, Harwell, in a flux of 10^{12} n $\times$ cm^{-2} $\times$ sec^{-1}. (The stone meteorites were ground to 400 mesh/cm^2 prior to irradiation; the siderites were irradiated in the form of clean cuttings). The Hf and Zr standards were prepared by evaporating dilute aqueous solutions of $HfOCl_2$ and $ZrOCl_2$ respectively (1–5 μg) on 500 mg portions of "Specpure" Na_2SiO_3 powder. The hafnium and zirconium content of the Na_2SiO_3 was checked by blank experiments and found to be negligible.

The irradiated *iron meteorite* samples were dissolved in aqua regia containing 20 mg Zr carrier (for Hf as well as for Zr). The solution was evaporated to dryness on the steam bath, and the process repeated after adding 20 ml of 6 N HCl. The residue was dissolved in 30 ml of 2 N HCl and the Hf and Zr extracted twice for 5 minutes with 15 ml of a 0·5 molar solution of TTA in xylene. (F. L. MOORE, 1956). The organic layer was washed twice with 10 ml of a mixture of 0·3 N HNO_3 + 0·3 N H_2F_2. To this solution 15 ml concentration HNO_3 and 10 ml concentrated H_2F_2 were added, along with 5 mg of Ta carrier. After cooling the solution to about 20°C, Hf and Zr were precipitated with an excess of saturated $Ba(NO_3)_2$ solution. The precipitated $BaHfF_6$ and $BaZrF_6$, respectively, were dissolved in HNO_3 saturated with H_3BO_3 and from the clear solution both the elements were precipitated as hydroxides by adding NH_4OH. After centrifuging and dissolving them in 4 N HCl,

holdback carriers of Fe, La, Ni, Ba and Na were added and the hafnium and zirconium precipitated with phenylarsonic acid. The precipitates were collected on filter paper and mounted for γ-scintillation counting. The chemical yields were determined by igniting the samples to the oxide; they ranged from 50–80 per cent.

Table 1. Results of Hf and Zr determinations in meteorites by neutron activation analysis

Sample	Run No.	Zr-concentration (p.p.m.)		Hf-concentration (p.p.m.)		Ratio (Zr/Hf)
Stone meteorites						
Plainview, Texas	1	36		1·9		
(Veined intermediate chondrite)	2	32	33 ± 4	1·5	1·7 ± 0·4	19·4
	3	30		2·1		
Morland, Kansas	1	31		2·3		
(Crystalline chondrite)	2	40	36 ± 5	1·5	1·8 ± 0·5	20·0
	3	38		1·6		
Potter, Nebraska	1	45		2·2		
(Brecciated chondrite)	2	52	48 ± 5	1·8	2·0 ± 0·4	22·4
	3	47		1·9		
Pultusk, Poland	1	28		1·1		
(Chondrite)			30 ± 4		1·2 ± 0·2	25·0
	2	32		1·3		
Mocs	1	18		0·48		
(Chondrite)			20 ± 4		0·44 ± 0·08	44·5
	2	23		0·39		
Iron meteorites						
Canyon Diablo	1	ca. 0·4		0·02		
	2			0·03	0·02 ± 0·02	ca. 20
	3			0·01		
Henbury	1			0·01		
	2	ca. 0·3		0·02	0·02 ± 0·02	ca. 20
	3			0·02		

For the analysis of the *stone meteorites* and the standards, the irradiated material was decomposed with $H_2F_2 + HClO_4$. Again 20 mg of Zr carrier was added to each sample. After all SiO_2 had been volatilized, the remaining solution was evaporated to complete dryness. A few ml of concentrated HNO_3 were added to oxidize iron to the trivalent state and the solution was again brought to dryness.

The extraction of hafnium and zirconium at this stage of the analysis proved impracticable. Therefore both the elements were first precipitated from $HNO_3 + H_2F_2$ solution as $BaHfF_6$ and $BaZrF_6$ respectively by adding an excess of $Ba(NO_3)_2$ solution. After dissolving the precipitate as described above, the Hf and Zr were reprecipitated as hydroxides. To remove all traces of F^- ions the hydroxides were reprecipitated once more. The hafnium and zirconium could now be extracted with

a 0·5 molar TTA solution in xylene and the further analysis continued as described for the iron meteorites.

At the time of completing the chemical analysis (about 25 days after the end of the irradiation) the radioactive nuclides still present in the samples were Hf^{175} ($T_{1/2}$ = 70 d); Hf^{181} $T_{1/2}$ = 46 d); Zr^{93}($T_{1/2} = 9 \times 10^5$ y) and Zr^{95} ($T_{1/2}$ = 65 d).

The γ-ray peak of Zr^{95} at 0·76 MeV was used for measuring the zirconium, using a 2 in. × 2 in. NaI crystal mounted on a photomultiplier tube. The pre-amplified pulses were fed into a 100-channel pulse height analyzer. None of the other 3 nuclides emits γ-rays with energies greater than 0·61 MeV and cannot therefore interfere with the measurement. The threshold of the pulse height analyzer was set to 0·70 MeV, so that only the 0·76 MeV γ-rays of Zr^{95} were counted with an external scaler. By comparison with the Zr standards, the Zr content of the samples were calculated. Then the Hf^{181} activity was measured by means of its 0·61 MeV γ-rays by setting the threshold of the analyzer at 0·55 MeV (Zr^{93} and Hf^{175} do not interfere). The Zr^{95} activity was subtracted from the total activity at this setting and from the remaining activity the amount of hafnium present in the samples could be calculated by comparison with the Hf standards.

The results of the measurements are given in Table 1.

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